PATENT SPECIFICATION

DRAWINGS ATTACHED

COMPLETE SPECIFICATION

Electrically Conductive Arrangements capable of Exhibiting the Thermo-electric or Peltier Effect

We, SIEMENS & HALSKE AKTIENGESELL-SCHAFT, a German Company of Berlin and Munich, Germany, do hereby declare the invention, for which we pray that a patent may
5 be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to electrically conductive arrangements capable of exhibiting
10 the thermo-electric or Peltier-effect.

For the technical utilisation of the thermo-electric effect (Seebeck-effect) as well as for the utilisation of the reversed effect, the so-called Peltier-effect, the necessity arises again
15 and again, to produce materials the thermal conductivity of which is small and the electrical conductivity and thermal power of which are as large as possible.

It is known to make the heat conductivity
20 small by using for instance materials with a small modulus of elasticity, i.e. materials consisting of heavy atoms and ions. A low conductivity of heat is also to be expected for crystals with a large coefficient of thermal
25 expansion. Moreover, crystals are known in which the heat conductivity has been reduced by the introduction of neutral atoms or by the formation of mixed crystals. Through the difference in the wavelength of electrons and
30 the so-called phonons, which correspond to the grid oscillation propagated in the crystal in the same way as photons to the light waves, only photons are diffracted by suitable inhomogeneities in the grid, whereas the mobility
35 of the electrons, and therefore the electrical conductivity of the substance, remains practically unchanged.

In the substances known so far one obtains, therefore, the required low thermal conduc-
40 tivity by a suitable choice of, or control over, the crystal grid, respectively. The invention proposes a totally new method of utilising the wave-mechanical tunnel effect.

The invention consists in an electrically

conductive arrangement including two elec- 45
trically conductive members in mutual contact and capable of exhibiting the thermo-electric or Peltier effect, at least one of which members or Peltier effect, at least one of which members consists of a substance including a plurality 50
of particles separated by, and in contact with, a material normally electrically insulating or electrically poorly conductive, wherein the particles consist of a semi-conductor material doped with an impurity and wherein the spac- 55
ing between the particles is such that whereas the thermal conductivity of at least that portion of the material located between the particles remains substantially constant the said portion is electrically conductive to an 60
extent greater than that corresponding to the specific conductivity of the material, and wherein the Lorenz number of the substance is low compared with the Lorenz number of the particles. 65

The term "semi-conductor" is used herein to define a class of crystalline substances having a valence band fully occupied at absolute zero temperature and an intrinsic conductivity band unoccupied at absolute zero tem- 70
perature (said bands being separated by a prohibited zone), wherein at working temperatures electrons migrate from the valence band to the intrinsic conductivity band to make the substance intrinsically conductive, or from the 75
valence band to impurity levels to make the substance p-conductive, or from impurity levels to the intrinsic conductivity band to make the substance n-conductive.

A more detailed description of preferred 80
embodiments of the invention is given in the following description.

Referring now to Figure 1, a potential wall, assumed here to be rectangular, is represented, as it is known from the physics of 85
the nucleus of the atom. The energy E is the ordinate, and the co-ordinate of the locus r is the abscissa. A particle of energy E_0 which is insufficient to pass over the potential

wall, can pass through this wall with a certain probability; it can do this the easier, the smaller the thickness d of the potential wall. Penetration of the potential wall can just be achieved if its thickness d lies in the order of magnitude of the mass wavelength of the particle moving towards the wall.

The basic idea of the invention is illustrated in Figure 2. An arrangement is shown which is composed of two electrically conductive elements in particular two semi-conductor elements, and an electrically insulating or electrically poorly conductive intermediate layer, with the characteristic that the intermediate layer has a thickness of approximately 5 to 100 A units, so that electrical conductivity occurs between the two electrically conductive elements 1 and 3 on account of the wave-mechanical tunnel effect, i.e. that the electrical conductivity of the intermediate layer 2 is considerably larger than that corresponding to the specific conductivity of the intermediate layer, whereas its heat conductivity remains practically unchanged. Particles which come from 1 or 3, come up against a potential wall caused by the intermediate layer 2 of thickness c, through which electrons with a wavelength of the order of magnitude of 100 A units may readily pass.

Phonons, however, the wavelength of which is of the order of a few grid constants i.e. of about 10 A units, will also penetrate this layer if the thickness thereof is at the lower of the said values since the probability with which phonons can penetrate through a layer having a thickness of 10 A units increases exponentially with decreases in thickness below this value. Therefore, for intermediate layer thicknesses of the order of say 5 A units, the change in thermal conductivity is still relatively small so that a favourable relationship between the electrical and thermal conductivities is produced even with layer thicknesses of the latter mentioned order.

The intermediate layer 2 has thus become conductive for the electric current on account of the wave-mechanical tunnel effect, whereas its heat conductivity, which is known to be low for insulators, remains practically unchanged. The conductor 4, is, therefore, electrically connected to the wall 1 through the plate 3 and the intermediate layer 2. The intermediate layer 2 only functions then as a heat insulator.

In accordance with the principle illustrated in Figure 2, an electrically conductive substance may be constructed consisting of an electrically insulating or electrically poorly conductive carrier substance in which is embedded particles of semi-conductor material, doped with an impurity, in a very fine and very even distribution, e.g. as a powder. The electrically conductive substance has the characteristic that, by the choice of the plurality of the particles suspended in the carrier

substance per unit volume, the Lorenz number $\lambda/\kappa T$ of the electrically conductive substance is reduced, in particular by about 10% or more, compared with the Lorenz number of the electrically conductive particles. The electrical conductivity of the first mentioned substance is, therefore, dependent on the shape, size and distribution of the particles in the carrier substance. The Lorenz number is defined as the ratio of the heat conductivity λ to the electrical conductivity κ, and it is an object of the present invention to make this ratio as small as possible, i.e. to reduce the Lorenz number of the electrically conductive substance.

Figure 3 represents the magnified junction of a thermo-couple illustrated in Figure 4. The particles embedded in the carrier substances 10 and 11 are separated from each other by a distance b which lies between 5 and 100 A units. The electrically insulating or poorly conductive carrier substances may be, for instance, organic varnishes, synthetic materials, inorganic insulators, glass or ceramic materials.

There are various possibilities for producing the distance between the suspended particles which is favourable for the manifestation of the tunnel effect. The carrier substance may, for instance, have a large electrical dipole moment. The particles suspended in the carrier substance are then charged approximately equally so that repelling Coulomb forces act upon them. At a certain distance between the embedded particles, which is approximately between 5 and 100 A units, the forces are balanced, and if the concentration of suspended particles in the carrier substance is suitable one can achieve a distance between the particles which is favourable for the tunnel effect to occur. The required distribution can also be obtained, for instance, by mechanical high-frequency vibrations by means of supersonic waves. In this case, too, the suspended particles are charged and, with a suitable concentration of suspended particles, a balance of forces again occurs at a distance therebetween favourable for the tunnel effect to occur.

The charged particles of the suspension may alternatively be spaced at the aforesaid distance by applying a potential across a conductor which consists of the carrier substance containing the suspended particles. The charged particles migrate then along the resulting voltage gradient, as is known from the so-called electrophoresis, and the required distribution of the particles in the carrier substance can be produced.

Semi-conductors cover themselves easily with a relatively thick, non-conductive oxide skin, so that the small distance required for the appearance of the wave-mechanical tunnel effect may not be obtained any more. However, the formation of this oxide skin can be

prevented by a thin coating (approximately mμ) of precious metal or precious metal alloy. The previous metal coating must be very thin since it acts as an electrical shunt which tends to deteriorate the electrical properties of the substance.

Alternatively, it is also possible to produce the distance favourable for the manifestation of the wave-mechanical tunnel-effect by means of these oxide skins if the thicknesses thereof are suitable.

Alternatively, chemical compounds, e.g. fluorides, hydrides, carbides or nitrides, may be produced on the surface of the semi-conductor particles in a suitable atmosphere, and the thickness of the coating formed by the chemical compound may be chosen so that the particles have the required distance between their electrically conductive nuclei even if they touch each other.

The required distance between the electrically conductive particles may alternatively be produced by a sintering process in a suitable atmosphere or in a vacuum, and/or by compression under high pressure. When sintering is effected care must be taken not to destroy the isolating intermediate layers, e.g. oxides, fluorides, hydrides, carbides and nitrides.

A further reduction in the Lorenz number of the electrically conductive substance that is, the carrier substance and the particles, can be achieved by embedding small gas bubbles in the suspension, so that it possesses a foamy or porous consistency, as is usually present when produced by sintering.

The method suggested by the invention leads to a particularly large improvement of the thermo-electrical properties, i.e. a large reduction of the Lorenz number, if the electrically conductive particles have a large thermo-power and large electrical conductivity and in which the heat conductivity therein is caused essentially by the grid oscillations and only to a very small extent by the electrons. The reduction of the Lorenz number is greatest when the portion of the heat conductivity due to the grid of the electrically conductive substance is made equal to the electron heat conductivity of this substance through the suitable choice of the distance between the particles suspended therein. This is explained in more detail by the following consideration:—

If L is the Lorenz number of a thermo-electrical material with large thermo-power and large grid heat conductivity λ_g, which is used as the particle material, and this material has a small electron heat conductivity λ_n which corresponds to the electrical conductivity κ according to the Wiedemann-Franz-Lorenz law, then the Lorenz number L of the particles is given by:—

(1) $L = \lambda_o + \lambda_g / \kappa T$

where T is the absolute temperature.

The intermediate layers formed by the carrier substance and/or the aforesaid chemical compounds on the surface of the particles must lead to a reduction of the grid heat conductivity of the electrically conductive substance, that is, the carrier and the particles. The heat conductivity of this substance is given by $\lambda_z . \kappa^1$ is the electrical conductivity of the latter substance, which is electrically conductive on account of the tunnel effect, and to which corresponds an electron heat conductivity λ^1_o according to the law of Wiedemann-Franz and Lorenz. The Lorenz number L^1 of the electrically conductive substance is then given by:—

(2) $L^1 = \lambda^1_o + \lambda_z / \kappa^1 T$

Since, according to the Wiedemann-Franz-Lorenz law, it is always the case that:—

(3) $\lambda_o / \kappa T = \lambda^1_o / \kappa^1 T \approx 2.5 \times 10^{-8} V^2 / temp. (degrees)^2$

L^1 will always be small than L, if:—
            $\kappa^1 \approx \kappa$

since $\lambda_z < \lambda_g$.

The greatest reduction of the Lorenz number which can be obtained is given when the distance between the suspended particles is chosen such that $\lambda_z \approx \lambda^1_o$.

From equations (2) and (3)

(4) $L^1 \approx 2L_{Metal} \approx 5 \times 10^{-8} V^2 / temp. (degrees)^2$

The Lorenz number L is a constant for pure metals and is denoted in the above equation by the expression L_{Metal}.

The improvement in the thermo-electrical properties of the electrically conductive substances will become particularly evident if one considers the so-called work factor A of a thermocouple. It is given by the relation:—

$$A = \frac{\epsilon^2}{(\sqrt{L_1} + \sqrt{L_2})^2}$$

where ϵ is the thermo-power, and L_1 and L_2 are the Lorenz numbers of the materials of which the two branches of the couple consist. The thermo-power reaches more than 1000 μV/temp.(degrees) in arrangements according to the invention. If both branches of the couple consist of an electrically conductive substance the Lorenz number of which is L^1, as referred to above, then:—

$$A \approx \frac{\epsilon^2}{4L^1}$$

With the numerical value for L^1 obtained from equation (4) and a value for the thermo-power of $\epsilon \approx 500/\mu V/temp.(degrees)$, there results a work factor of approximately 1.3, whereas it is only 0.6 for the best thermo-couples known at present.

The following semi-conductor particles doped with an impurity, e.g. doped $A_{III}B_V$ compounds, silicon, silicon-carbide and germanium, are particularly suitable as substances with a large electrical conductivity and a large thermo-power as well as a large grid heat conductivity.

Doping may be accomplished in particular by diffusion; the semi-conductor powder, for instance, may be tempered for a sufficiently long time in a suitable atmosphere, e.g. boron or antimony vapour. Doping may, however, also be carried out together by a sintering process. For a large reduction of the Lorenz number it is favourable to use semi-conductor powder with as fine a grain as possible, in particular with particles not larger than $1\,\mu$.

In one embodiment, represented in Figure 4, a thermocell is shown in which, for instance, two branches 5 and 6 thereof are each made from an electrically conductive substance, wherein the particles introduced into the carrier substance of one branch have a large thermo-power compared with the particles suspended in the carrier substance of the other branch. If the two junctions 8 and 9 are at different temperatures T_1 and T_2, a thermo-current flows, which can be measured with the instrument 7.

The carriers may consist of the same or of different substances. In particular, one thermo-branch only may consist of an electrically conductive substance formed in a manner described above.

A further application of the latter substance is the use thereof as Peltier discs in a Peltier arrangement, as shown in Figure 5. The Peltier effect is a reversal of the thermo-electric or Seebeck effect, and arrangements for the utilisation of the Peltier effect put the same demand on the material as on thermo-electrical substances, i.e. large thermo-power, larger electrical conductivity, and small heat-conductivity, i.e. a small Lorenz number. In the embodiment of Figure 5 the Peltier "discs" are illustrated by the elements 12 and 13. The elements 12 consist, for instance, of metal, and the element 13 of an electrically conductive substance formed in a manner described above. Figure 6 is a magnified junction. If a current caused by the voltage source 16 flows through the arrangement of Figure 5, the junctions 14 and 15 rise to different temperatures T_3 and T_4. Alternatively all "discs" may consist of the latter mentioned substance.

WHAT WE CLAIM IS:—

1. An electrically conductive arrangement including two electrically conductive members in mutual contact and capable of exhibiting the thermo-electric or Peltier effect, at least one of which members consists of a substance including a plurality of particles separated by, and in contact with, a material normally electrically insulating or electrically poorly conductive, wherein the particles consist of a semi-conductor material doped with an impurity and wherein the spacing between the particles is such that whereas the thermal conductivity of at least that portion of the material located between the particles remains substantially constant the said portion is electrically conductive to an extent greater than that corresponding to the specific conductivity of the material, and wherein the Lorenz number of the substance is low compared with the Lorenz number of the particles.

2. An arrangement as claimed in Claim 1, wherein the Lorenz number of the said substance is lower than that of the particles by not less than 10%.

3. An arrangement as claimed in Claim 1 or Claim 2, wherein the said spacing between the particles is between 5 and 100 A.

4. An arrangement as claimed in any of Claims 1 to 3, wherein each of the said particles is not larger than $1\,\mu$.

5. An arrangement as claimed in any of Claims 1 to 4, wherein the particles are doped by a diffusion process.

6. An arrangement as claimed in any of Claims 1 to 5, wherein the electrically insulating or electrically poorly conductive material has a high electrical dipole moment.

7. An arrangement as claimed in any of Claims 1 to 6, wherein the electrically insulating or electrically conductive material is a carrier material and the particles are suspended therein.

8. An arrangement as claimed in Claim 7, wherein the process of placing the particles in suspension is effected by means of supersonic waves.

9. An arrangement as claimed in Claim 7, wherein the process of placing the particles in suspension is effected by means of electrophoresis.

10. An arrangement as claimed in any of Claims 7 to 9, wherein the suspended particles are coated with a layer, $1\,\mu$ thick, of a precious metal or previous metal alloy.

11. An arrangement as claimed in any of Claims 1 to 6, wherein the electrically insulating or electrically poorly conductive material is composed of chemical compounds of the the particle material.

12. An arrangement as claimed in Claim 11, wherein the electrically insulating or electrically poorly conductive material is composed of the oxide skins of the particle material.

13. An arrangement as claimed in any of Claims 1 to 12, wherein the mechanical rigidity of the said substance and/or the required spacing between the particles is produced by a sintering process and/or compression at high pressure.

14. An arrangement as claimed in any of Claims 1 to 13, wherein small gas bubbles are suspended in the said substance which bubbles give the substance a foamy or porous consistency.

15. An arrangement as claimed in any of Claims 1 to 14, wherein each of the said members consists of the said substance.

16. An arrangement capable of exhibiting the thermo-electric or Peltier effect substan-

tially as hereinbefore described with reference
to Figures 3 to 6 in the accompanying draw-
ing.

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1 SHEET

This drawing is a reproduction of
the Original on a reduced scale.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6